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(54) Title: SYNTHESIS OF N-VINYL FORMAMIDE

(57) Abstract: A process to produce N-vinylformamide includes the steps of reacting hydroxyethyl formamide with a reactant including at least one cyclic anhydride group to form an ester, and dissociating (or cracking) the ester to synthesize N-vinylformamide and a compound including at least one diacid group. The ester can be dissociated using heat. The reactant including at least one cyclic anhydride group can, for example, be succinic anhydride, maleic anhydride, phthalic anhydride, a polymer including at least one cyclic anhydride group, or a solid support to which at least one cyclic anhydride group is covalently tethered. Preferably, the cyclic anhydride is regenerated from the diacid formed in the synthesis of the ester by heating the diacid to dehydrate the diacid. The temperature required to dehydrate diacid groups is preferably higher than the temperature use to dissociate the ester.

SYNTHESIS OF N-VINYL FORMAMIDE

CROSS-REFERENCE TO RELATED APPLICATION

The present application claims benefit of U.S. Provisional Patent Application Serial No. 60/407,077, filed August 30, 2003, the disclosure of which is incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0001] The present invention relates to the synthesis of N-vinylformamide, and particularly, to the synthesis of N-vinylformamide using cyclic anhydride reagents.

[0002] N-vinylformamide (NVF) is a monomer with potentially useful properties in that it free-radically polymerizes to produce water-soluble poly(N-vinylformamide) (PNVF) and also undergoes controlled radical polymerization using RAFT methodology. Badesso, R. J.; Nordquist, A. F.; Pinschmidt, Jr. R. K.; and Sagl, D. J. "Hydrophilic polymers: performance with Environmental Acceptance", Glass, E.; Ed.; America Chemical Society, Washington, DC, 1995, p489. PNVF is probably the most practical precursor for preparation of poly(vinylamine). Because vinyl amine is unstable and hence cannot be maintained, PNVF is likely the best route to the generation of polyvinyl amine, a useful and less toxic alternative to polyacrylamide and other cationic, water-soluble polymers. PNVF is easily hydrolyzed under basic or acidic conditions to form poly(vinylamine).

[0003] There are three known commercial routes to NVF. For example, BASF, at its Ludwigshafen, Germany site, reacts acetaldehyde with HCN, then formamide, forming the cyanoethyl formamide (FAN). FAN is then "cracked" to NVF plus HCN, where the latter is recycled. The BASF Ludwigshafen, Germany site is one of the few sites in the world skilled in HCN chemistry. As this highly toxic chemical cannot be transported, the process is most likely restricted to Ludwigshafen.

[0004] Mitsubishi developed a process whereby acetaldehyde is reacted with formamide to form hydroxyethyl formamide (HEF) using either acid or base catalysis. HEF is then reacted with methanol to form methoxyethyl formamide (MEF) using an acid catalyst with the loss of water. HEF is finally cracked to methanol and NVF, and the NVF purified. It has been reported that the NVF material synthesized by this method, exhibited lower than desired purity.

[0005] Air Products developed an alternative route to NVF wherein HEF is reacted with additional formamide (over a solid acid catalyst) to form the ethylidene bisformamide (BIS) plus water. BIS is then cracked (pyrolyzed) to form NVF plus formamide (wherein the latter is recycled). The NVF is then vacuum distilled. It is quite important in the operation of this process to minimize the hydrolysis of formamide (creating ammonia that fouls the catalyst) during BIS formation. Obviously the presence of water during this reaction creates problems.

[0006] It is very desirable to develop alternative routes to the synthesis of N-vinylformamide.

SUMMARY OF THE INVENTION

[0007] In one aspect, the present invention provides a process to produce N-vinylformamide including the steps of: reacting hydroxyethyl formamide with a reactant including at least one cyclic anhydride group to form an ester, and dissociating (or cracking) the ester to synthesize N-vinylformamide and a compound including at least one diacid group. The ester can be dissociated using heat. The reactant including at least one cyclic anhydride group can, for example, be succinic anhydride, maleic anhydride, phthalic anhydride, a polymer including at least one cyclic anhydride group, or a solid support to which at least one cyclic anhydride group is covalently tethered. Preferably, the cyclic anhydride is regenerated from the diacid formed in the synthesis of the ester. The anhydride can, for example, be regenerated by heating the diacid to dehydrate the diacid or by passing the diacid over a dehydration catalyst. Homogeneous or heterogeneous dehydration catalysts can be used (for example, zeolite, resins acids, vanadium oxide, phosphoric oxide or any other dehydration catalyst as known to those skilled in the art). The conditions required to dehydrate diacid groups are preferably different from the conditions used to dissociate the ester. For example, in the case that heat is used to dehydrate the diacid, the temperature required for dehydration can be higher than the temperature used to dissociate the ester.

[0008] As used herein, the term "polymer" refers to a compound having multiple repeat units (or monomer units) and includes the term "oligomer," which is a polymer that has only a few repeat units. The term polymer also includes copolymers which is a polymer including two or more dissimilar repeat units (including terpolymers - comprising three dissimilar repeat units - etc.).

[0009] Although the reaction can be carried out without the use of solvent, a solvent can be added. Suitable solvents include aprotic or aromatic solvents. Preferably, such

solvents do not interfere with the reactions of the present invention. NVF can be used as a solvent in the process. Examples of other suitable solvents include, but are not limited to, toluene, xylene, acetonitrile, ether, dimethyl sulfoxide and/or acetaldehyde. Suitable solvents also include isoparaffin-like solvents, including, but not limited to, the products sold by Exxon Corporation under the name ISOPAR®, which are generally non-toxic in nature.

[0010] In one embodiment a solvent (for example, NVF) is used in which NVF is soluble and in which a polymer including at least one cyclic anhydride group is at least partially soluble. However, the polymer including at least one ester group formed in the synthesis and the polymer including at least one diacid group formed in the synthesis have no or limited solubility in the solvent.

[0011] Generally, polymers used in the process of the present invention preferably include or incorporate a plurality of cyclic anhydride groups. For example, a copolymer of methyl vinyl ether and maleic anhydride can be used. The methyl vinyl ether/maleic anhydride copolymer can, for example, have a weight average molecular weight in the range of approximately 190,000 to 3,000,000. The polymer can also be a reaction product of an alpha olefin or a mixture of alpha olefins with maleic anhydride. In one embodiment, the alpha olefin is a C-18 alpha olefin and the copolymer has a molecular weight of at least 20,000. The polymer can also be a methyl vinyl ether/ maleic anhydride/ decadiene copolymer. Another suitable polymer for use in the present invention is a copolymer of styrene and maleic anhydride. The styrene/maleic anhydride copolymer can, for example, have a weight average molecular weight of at least 2000.

[0012] In one embodiment the polymer is a solid in the reaction. For example, the polymer can be a porous crosslinked solid. Preferably, the porous polymer has a relatively high surface area.

[0013] In one embodiment in which the reactant including at least one cyclic anhydride group is a solid support to which at least one cyclic anhydride group is covalently tethered, the solid support is silica.

[0014] In another embodiment, acetaldehyde, formamide and the reactant including at least one cyclic anhydride group are mixed in a single reaction vessel, wherein hydroxyethyl formamide is formed in the reaction vessel to react with the reactant including at least one cyclic anhydride group.

[0015] In another aspect, the present invention provides a process to produce N-vinylformamide including the step of: mixing acetaldehyde, formamide and a source of anhydride in a single reaction vessel. The anhydride reacts with hydroxyethyl formamide

formed in the reaction vessel to form an ester as described above. The ester is dissociated (or cracked) as described above to synthesize N-vinylformamide and a compound including at least one diacid group. In one embodiment, the source of anhydride is a reactant including at least one cyclic anhydride group. The reactant including at least one cyclic anhydride group can, for example, be succinic anhydride, maleic anhydride, phthalic anhydride, a polymer including at least one cyclic anhydride group, or a solid support to which at least one cyclic anhydride group is covalently tethered. In one embodiment, the acetaldehyde to formamide mole ratio can, for example, be at least two. However, lower acetaldehyde to formamide mole ratios can be used. An acid or base catalyst can be used in the reaction to make hydroxyethyl formamide.

[0016] The process of the present invention can be carried out continuously or batchwise. Suitable reactors include, but are not limited to, tubular reactors and stirred tank reactors.

[0017] In still another aspect, the present invention provides a reagent including at least one cyclic anhydride group covalently tethered to a solid support. The solid support can, for example, be silica. Preferably, a plurality of cyclic anhydride groups are tethered to the solid support.

[0018] The present invention, along with the attributes and attendant advantages thereof, will best be appreciated and understood in view of the following detailed description taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] Figure 1 illustrates the sequential synthesis of NVF via first synthesizing HEF. reacting HEF with acetic anhydride and cracking the resulting ester to form NVF.

[0020] Figure 2 illustrates a one pot synthesis of NVF of the present invention wherein acetaldehyde, formamide and acetic anhydride are mixed.

[0021] Figure 3A illustrates an embodiment of a synthetic route to NVF of the present invention wherein a cyclic anhydride is reacted with HEF to form an HEF-adduct, which is subsequently cracked to form NVF.

[0022] Figure 3B illustrates a sequential synthesis under the general synthetic route of Figure 3A.

[0023] Figure 3C illustrates a one-pot synthesis under the general synthetic route of Figure 3A.

[0024] Figure 4 illustrates an embodiment of a synthetic route of the present invention in which a poly(styrene-co-maleic anhydride) copolymer is reacted with HEF.

[0025] Figure 5A illustrates a cyclic anhydride covalently tethered to a solid support for use in the synthetic methods of the present invention.

[0026] Figure 5B illustrates one embodiment of a synthetic route to the synthesis of a silica supported cyclic anhydride.

DETAILED DESCRIPTION OF THE INVENTION

[0027] Figure 1 illustrates a sequential synthesis of NVF developed at Air Product wherein HEF is first synthesized via the reaction of acetaldehyde and formamide. See Parris, G.E. and Armor, J.N, Applied Catalysis, Vol. 78, pp 65-78 (1991). HEF is then reacted with acetic anhydride to form an HEF adduct. The resulting HEF adduct/ester is subjected to heat (cracked) to form NVF.

[0028] The present inventors have discovered that NVF can also be formed via a single reaction mixture including acetaldehyde, formamide and an anhydride such as acetic anhydride as illustrated in Figure 2. The resulting HEF adduct is cracked to form NVF. The one-pot or single reactor synthesis of the present invention can, for example, provide cost savings by reducing unit operation costs. As expected from studies of the sequential synthetic route, the reaction rate increased in the one-pot synthesis with increasing temperature. As monitored by IR, for example, the anhydride peak was found to disappear in 42 hours at room temperature (approximately 22°C), in 23 hours at 50°C, and in 7.5 hours at 100°C, in the sequential synthesis. IR analysis of a one-pot synthesis according to Figure 2 also demonstrated disappearance of the anhydride peak over time. The temperature of the reaction of the present invention is generally approximately 0°C to 150°C, preferably approximately 20°C to 100°C, and more preferably approximately 30 to 80°C. In the studies of the present invention, a reaction temperature in the range of approximately 30°C to approximately 80°C was used. Either an acid catalyst or a base catalyst can be used. If an acid catalyst is used, only a catalytic amount of acid is preferably added to the reaction mixture (for example, 0.001 – 0.2 times the stoichiometry to HEF). Example of suitable acid catalysts include, but are not limited to, sulfuric acid, paratoluenesulfonic acid, methane sulfonic acid, amberlyst or any other acidic ion exchange resin. If a base catalyst is used, a nearly stoichiometric amount of base can be required (for example, 0.2 to 5 times the stoichiometry to HEF). Suitable homogeneous catalyst for use in the present invention

include, but are not limited to, triethylamine, pyridine and caustic catalysts. In general, any basic ion exchange catalyst such as Amberlite, Lewatit, Puralit is also suitable. Basic zeolites can also be suitable in certain cases.

[0029] In each of the synthetic routes of Figure 1 and 2, however, two moles of acetic acid are produced during the synthesis of one mole of NVF. One mole of acetic acid is produced in the synthesis of the HEF adduct, and another mole of acetic acid is produced during cracking of the HEF adduct. Acids such as acetic acid destabilize NVF. Moreover, the removal of such acids via, for example, distillation is difficult as the relative volatilities of the acid and NVF are similar.

[0030] In another aspect of the present invention as illustrated, for example, in Figures 3A through 3C, an alternative route to the synthesis of NVF is provided in which a cyclic anhydride is reacted with HEF. In the synthetic route of the present invention, HEF is reacted with a cyclic anhydride to form the corresponding ester (HEF adduct). The ester is then cracked to NVF plus the corresponding diacid under very mild conditions (for example, temperatures less than 25°C). The temperature of cracking is generally approximately 0°C to 250°C, preferably approximately 20°C to 200°C, and more preferably approximately 60 to 180°C.

[0031] While one can form NVF from a simple, non-cyclic anhydride (for example, acetic anhydride as illustrated in Figures 1 and 2), this reaction produces a very soluble acid byproduct which ultimately destabilizes the NVF as described above. Once again, the removal or separation of the resultant acids using non-cyclic anhydrides is very difficult. In the synthetic route of the present invention, relatively heavy cyclic anhydrides (many of which are commercially available or readily synthesized from commercially available reagents) are reacted with HEF to produce the corresponding HEF adduct and a diacid. No byproduct is produced. The diacid generated during the cracking step is generally less soluble than, for example, acetic acid formed in the synthetic route of Figures 1 and 2. Indeed, in several embodiment of the present invention in which a solubilized source of cyclic anhydride is used, the diacid may precipitate as a solid as it is formed. Examples of cyclic anhydrides suitable for use in the synthetic processes of the present invention include maleic anhydride, succinic anhydride and phthalic anhydride (the structures of which are set forth in Figure 3A).

[0032] The diacid formed in the synthesis of the present invention can be recycled and dehydrated to reform the anhydride. This recycling dehydration step can generally occur at a temperature higher than the temperature used to crack the HEF adduct and results in the

formation of water. The temperature of the dehydration is generally approximately 100°C to 450°C, preferably approximately 120°C to 300°C, and more preferably approximately 150 to 250°C. A dehydration catalyst can also be used to lower the temperature of dehydration, but is preferably not present in the cracking step to avoid the undesirable formation of water when NVF is formed. Suitable dehydration catalysts include homogeneous and heterogeneous catalysts (for example, zeolite, resins, acids, vanadium oxide, phosphoric oxide and any other dehydration catalyst as known to those skilled in the art). Unlike several current synthetic routes to NVF, the water produced in the recycling step of the present invention is formed "offline" and will not result in hydrolysis of the formamide precursor or the NVF product. Moreover, the synthetic route of the present invention requires less stringent conditions than current synthetic routes and hence can provide a product of increased purity. NVF of increased purity, for example, allows for generation of higher molecular weight poly(NVF)).

[0033] Various "substituted" cyclic anhydrides can be used in the synthetic route of the present invention to further decrease any adverse effects upon the NVF product of the diacid produced in the synthesis of the present invention. Generally, the use of such substituted cyclic anhydrides preferably reduces the solubility of the resulting diacid in the process solvent and/or facilitates the separation of that diacid from the NVF product. For example, in one embodiment a polymeric material including cyclic anhydride groups can be reacted with HEF. In the embodiment of Figure 4, for example, a copolymer of styrene and maleic anhydride was used as the source of cyclic anhydride. In this embodiment, the cracking reaction produced liquid NVF and generally insoluble or reduced solubility polymer including diacid groups.

[0034] Polymers including cyclic anhydride groups for use in the present invention can be soluble in a solvent in which the reaction is carried out. As HEF is a solid at room temperature, the adduct of HEF and the anhydrides used in the present invention may in some cases also be a solid. Thus, the use of a solvent/co-solvent may be required. As any solvent used in the processes of the present invention is typically ultimately required to be separated from the NVF product, it is advantageous to use NVF as a process solvent in the reactions of the present invention. In using NVF as the process solvent, a recycle stream can be taken from an intermediate point in the process to provide the needed solvent. In the case that a soluble polymer including cyclic anhydride groups are used, the resulting polymer containing diacid groups preferably readily precipitates from solution (for example, upon formation or upon addition of a co-solvent or other additive) and/or is preferably readily otherwise

separable from the NVF product. Separation of the polymer including diacid groups from NVF is typically readily achieved given the substantial difference in molecular weight between NVF and the polymer including diacid groups.

[0035] Because of the great difference in the volatilities of the diacid and NVF, it is possible, for example, to separate the monomer by a short residence time flash stripping leading to an enhanced quality of monomer. Melt crystallization can also be used to separate the monomer from a third solvent used to remove the diacid. Conditions of cracking (temperature and vacuum) can also be adjusted to flash the monomer as soon as it is formed. If the solid ester is heated at, for example, 150°C and 2mm Hg, NVF will naturally be formed in a gaseous state and can be condensed as pure NVF in another vessel.

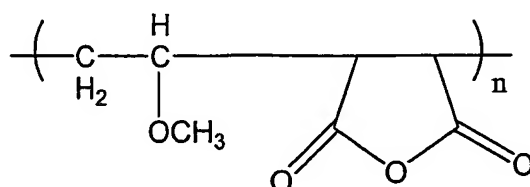
[0036] Additionally, polymers including cyclic anhydride groups that are insoluble in the process solvent (for example, solid polymers) can also be used in the present invention. As reactions of HEF with such insoluble polymers will occur only at the surface of the polymer, the surface area of such polymer is preferably relatively high. Such polymers can, for example, be synthesized as porous polymeric beads in a manner similar to the synthesis of, for example, polymeric ionic exchange beads as known in the art. In one embodiment, for example, divinyl benzene can be used as a crosslinker in a copolymer of divinyl benzene, styrene and maleic anhydride to produce a high surface area, porous polymer bead including cyclic anhydride groups for use in the reactions of the present invention. Preferably, the surface area is maximized. A surface area of, for example, at least 10 m²/g is preferred. As the resulting diacid is covalently bound to the solid polymer, the detrimental effect of the diacid groups upon the NVF product is not substantial.

[0037] As illustrated in, for example, Figure 5A, in another embodiment of the present invention, cyclic anhydride reagents for use the present invention can be immobilized upon a solid support (for example, a polymeric bead or a silica support). Figure 5B illustrates one embodiment of immobilization of a cyclic anhydride group on silica. Supports other than silica (for example, glass, alumina and activated carbon can also be used to immobilize the cyclic anhydride reagents of the present invention.

[0038] The cyclic anhydrides of the present invention can be reacted in either a sequential synthesis or a one-pot synthesis to form NVF as described above. In the generalized formula of a cyclic anhydride suitable for use in the present invention, R¹ and R² can independently be chosen from a very broad range of substituents. It is believed that electron withdrawing groups (for example, NO₂, halo group (for example, Cl, F or Br) and -CN) may result in a faster reaction time. In the case that a polymer including or

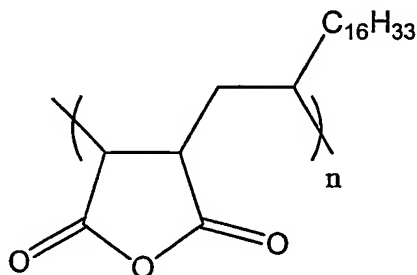
incorporating cyclic anhydride groups is used, R^1 and R^2 can, for example, be styrene or vinyl repeat groups. Virtually any vinyl monomer (for example, vinyl ether) is suitable for use in synthesizing polymers suitable for use in the present invention. Maleic anhydride typically copolymerizes in an alternative fashion. Thus R^1 and R^2 can be the same in the case of copolymerization of maleic anhydride. Styrene is an attractive comonomer as formation of crosslinked porous beads is readily achieved using styrene as a comonomer.

[0039] A number of polymeric anhydrides suitable for use in the present invention are commercially available. For example, a methyl vinyl ether/maleic anhydride copolymer is available from ISP Chemicals under the name GANTREZ® in the molecular weight range of 190,000 to 3,000,000. The polymer has the general formula:



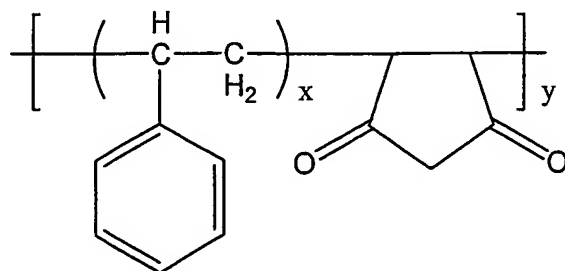
A methyl vinyl ether/maleic anhydride decadiene crosslinked polymer is also available from ISP Chemicals under the name STABILEZE®.

[0040] A copolymer of a C-18 alpha olefin with maleic anhydride have the following formula:



is available from Chevron Phillips under the produce name PA-18 Polyanhydride Resin.

[0041] Styrene maleic anhydride copolymers having the general formula:



are available, for example, from Sartomer of Exton, PA.

[0042] Experimental Examples

[0043] In the studies of the present invention, some of the quantities were varied between experiments but the quantities set forth in the examples below are representative values and scales. No attempt was made to optimize any of the reactions studied.

[0044] (1) One-pot reaction of acetaldehyde, formamide and acetic anhydride

[0045] i) No solvent: Acetaldehyde [21ml; 0.377mol], formamide [5ml; 0.126mol; containing 0.5mol% K₂CO₃] and acetic anhydride [6ml; 0.062mol] were added to a flask and stirred at approximately 10°C for 2h. The reaction was allowed to warm to room temperature over 1h and then heated to 70°C. IR monitoring was done throughout, demonstrating disappearance of the anhydride peaks and indicating the synthesis of the HEF adduct.

[0046] ii) With solvent: The same method as i) was followed but in addition, 40ml of isooctane was added at the start of the reaction. Two layers were present throughout the reaction. IR monitoring was done throughout, demonstrating disappearance of the anhydride peaks and indicating the synthesis of the HEF adduct.

[0047] (2) Production of NVF using poly(styrene-co-maleic anhydride)

[0048] Sequential addition: Acetaldehyde [5.66ml; 0.10mol] was dissolved in dioxane [20ml] at 10°C. Formamide [01ml; 0.025mol; containing 0.5mol% K₂CO₃] was added dropwise, and the reaction was stirred at 10-15°C for 2h. Poly(styrene-co-maleic anhydride) [68wt% styrene; Mn~1700] [8.29g] was dissolved in dioxane [50ml] and the solution added to the reaction. IR monitoring was done throughout the reaction. Anhydride peaks substantially reduced but did not completely disappear in IR over the time the reaction was carried out. Synthesis of NVF was confirmed by NMR.

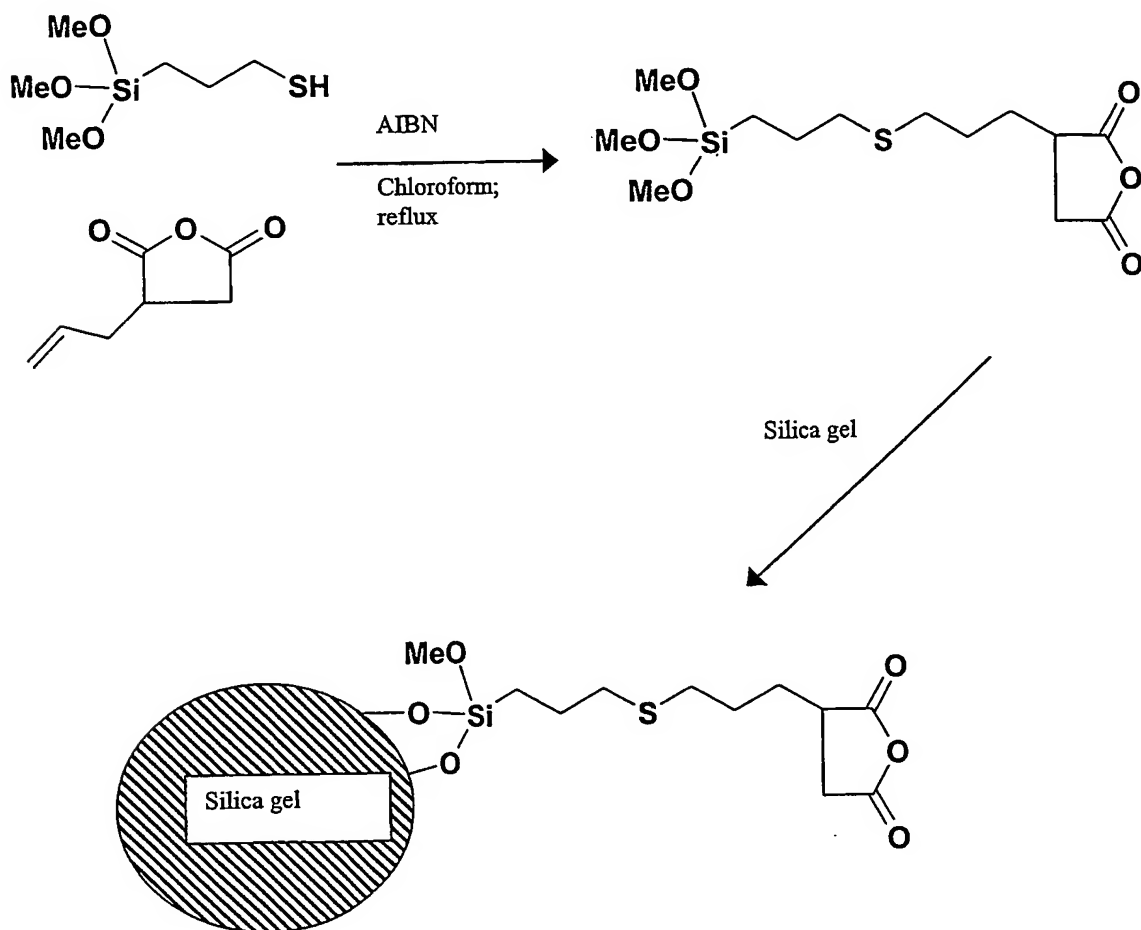
[0049] (3) Preparation of tethered anhydride

[0050] i) As illustrated in Scheme 1 below, Allylsuccinic anhydride [0.67g; 0.005mol], (3-mercaptopropyl-trimethoxysilane [2.8g; 0.014mol] and AIBN [50mg] were dissolved in chloroform [60ml] and refluxed overnight. Solid product was filtered off, and the solvent was removed from the filtrate to leave a yellow oil.

[0051] ii) The product from i) was added to a stirred suspension of silica gel [8g; surface area ~500m²/g] in toluene [200ml] and stirring was continued at room temperature for approximately 20h. The silica (i.e. tethered anhydride) was then filtered off and washed with toluene.

[0052] (4) Reaction of tethered anhydride

[0053] HEF and the tethered anhydride were reacted at 80°C in dioxane. The silica support was then filtered from the reaction mixture. The remaining reaction components were then heated at 100°C for approximately 6 hours.



Scheme 1

[0054] The foregoing description and accompanying drawings set forth the preferred embodiments of the invention at the present time. Various modifications, additions and alternative designs will, of course, become apparent to those skilled in the art in light of the foregoing teachings without departing from the scope of the invention. The scope of the invention is indicated by the following claims rather than by the foregoing description. All changes and variations that fall within the meaning and range of equivalency of the claims are to be embraced within their scope.

WHAT IS CLAIMED IS:

1. A process to produce N-vinylformamide including the steps of: reacting hydroxyethyl formamide with a reactant including at least one cyclic anhydride group to form an ester, and dissociating the ester to synthesize N-vinylformamide and a compound including at least one diacid group.
2. The process of Claim 1 wherein the reactant including at least one cyclic anhydride group is succinic anhydride, maleic anhydride, phthalic anhydride, a polymer including at least one cyclic anhydride group, or a solid support to which at least one cyclic anhydride group is covalently tethered.
3. A process of claim 1 wherein the cyclic anhydride is regenerated from a diacid formed in the synthesis of the ester by dehydrating the diacid.
4. The process of claim 1 where NVF is used as a solvent.
5. The process of claim 1 where toluene or acetaldehyde is used as a solvent.
6. The process of claim 2 wherein a polymer including at least one cyclic anhydride group is used.
7. The process of claim 6 further including the step of regenerating the polymer including at least one cyclic anhydride group by heating the polymeric material containing at least one diacid group to a temperature sufficiently high to dehydrate diacid groups.
8. The process of claim 7 wherein the temperature used to dehydrate diacid groups is higher than a temperature use to dissociate the ester by heat.
9. The process of claim 6 where NVF is used as a solvent.
10. The process of claim 6 where toluene or acetaldehyde is used as a solvent.
11. The process of claim 6 where a solvent is used in which NVF is soluble and in which the polymer including at least one cyclic anhydride group, the polymer including at least one ester group and the polymer including at least one diacid group having no or limited solubility in the solvent.

12. The process of claim 6 where polymer includes a plurality of cyclic anhydride groups and is a copolymer of methyl vinyl ether and maleic anhydride.
13. The process of claim 12 where in the methyl vinyl ether/maleic anhydride copolymer has a weight average molecular weight in the range of approximately 190,000 to 3,000,000.
14. The process of claim 6 wherein the polymer is a reaction product an alpha olefin or a mixture of alpha olefins with maleic anhydride.
15. A process of claim 14 the alpha olefin is a C-18 alpha olefin and wherein the polymer has a molecular weight of at least 20,000.
16. The process of claim 6 where the polymer is a methyl vinyl ether/ maleic anhydride decadiene copolymer.
17. The process of claim 6 wherein the polymer is a copolymer of styrene and maleic anhydride.
18. The process of claim 16 wherein the copolymer has a weight average molecular weight of at least 2000.
19. The process of claim 6 wherein the polymer is a solid in the reaction.
20. The process of claim 19 wherein the polymer is a porous crosslinked solid.
21. The process of claim 20 wherein the polymer is a crosslinked polymer including styrene and maleic anhydride repeat units.
22. The process of claim 2 wherein the reactant including at least one cyclic anhydride group is a solid support to which at least one cyclic anhydride group is covalently tethered.
23. The process of claim 22 wherein the solid support is silica.
24. The process of claim 1 wherein acetaldehyde, formamide and the reactant including at least one cyclic anhydride group are mixed in a single reaction vessel, hydroxyethyl formamide being formed in the reaction vessel to react with the reactant including at least one cyclic anhydride group.

25. A process to produce N-vinylformamide including the steps of: mixing acetaldehyde, formamide and a source of anhydride in a single reaction vessel, dissociating an ester formed by a reaction between the source of anhydride and hydroxyethyl formamide formed in the reaction vessel to synthesize N-vinylformamide and a compound including at least one diacid group.

26. The process of claim 25 wherein the source of anhydride is a reactant including at least one cyclic anhydride group.

27. The process of Claim 26 wherein the reactant including at least one cyclic anhydride group is succinic anhydride, maleic anhydride, phthalic anhydride, a polymer including at least one cyclic anhydride group, or a solid support to which at least one cyclic anhydride group is covalently tethered.

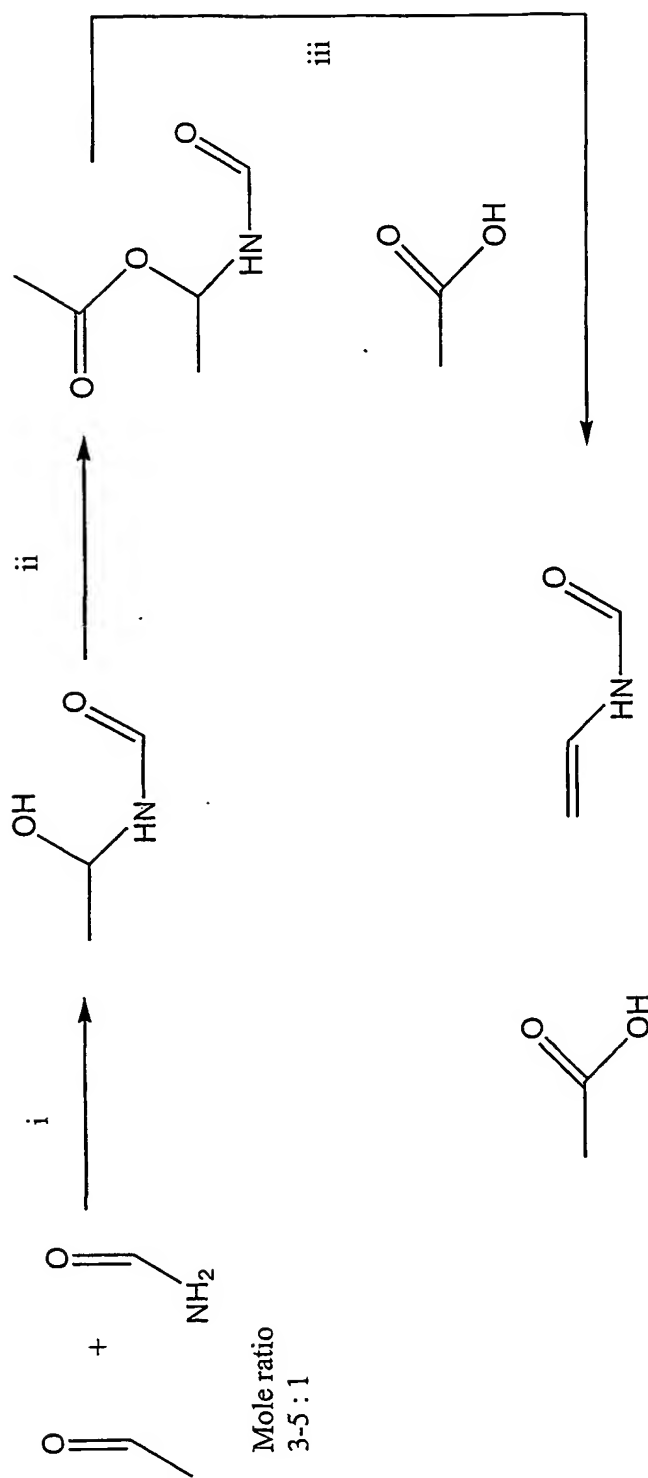
28. The process of Claim 25 wherein the acetaldehyde to formamide mole ratio is at least two.

29. A process of claim 25, where a base or an acid catalyst is used in the reaction to make hydroxyethyl formamide.

30. A reagent comprising at least one cyclic anhydride group covalently tethered to a solid support.

31. The reagent of claim 30 where the solid support is silica.

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i. K_2CO_3 (0.5 mol% cf. Formamide); 10-15 C; 3-4 h

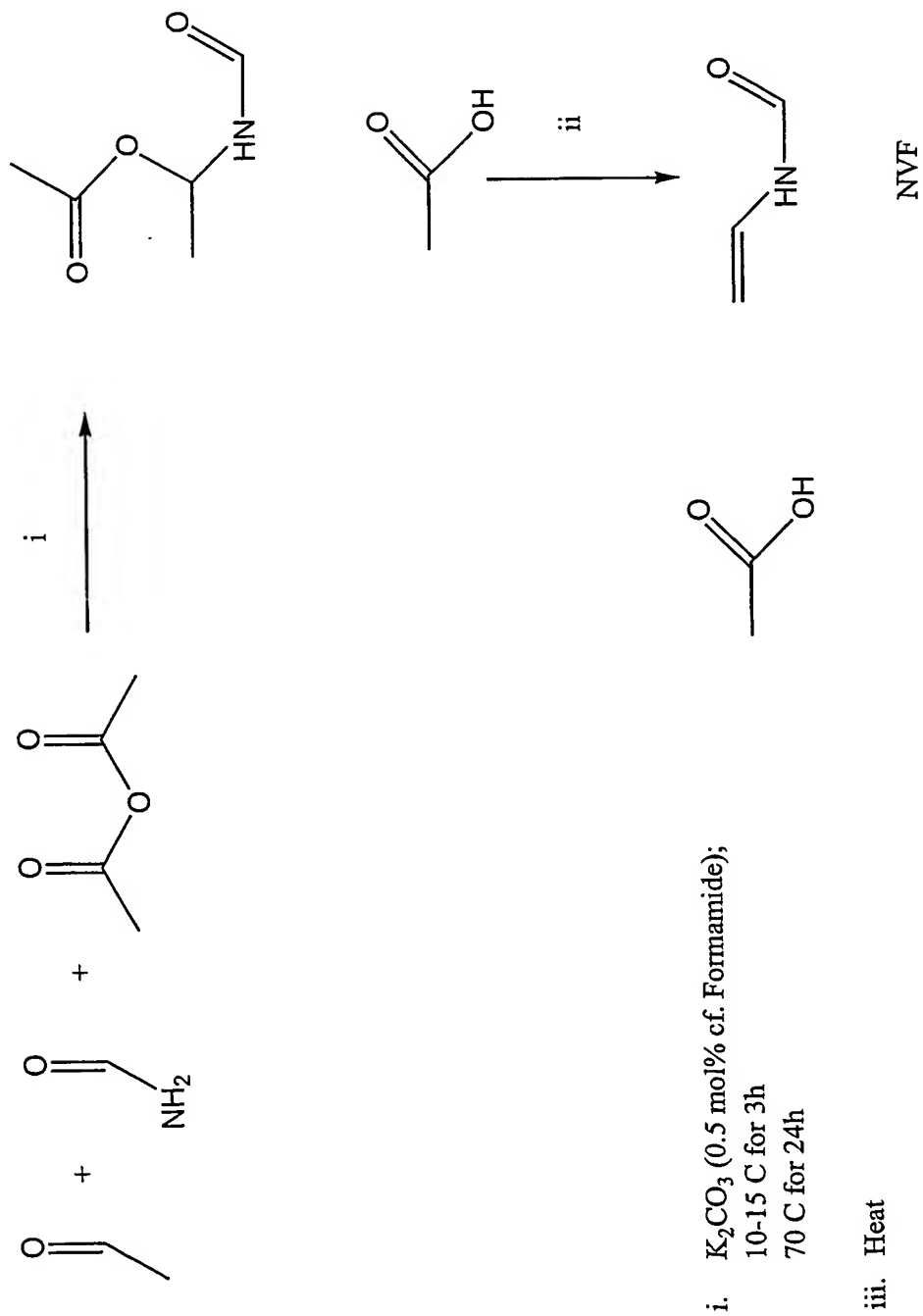
NVF

ii. Acetic Anhydride

iii. Heat

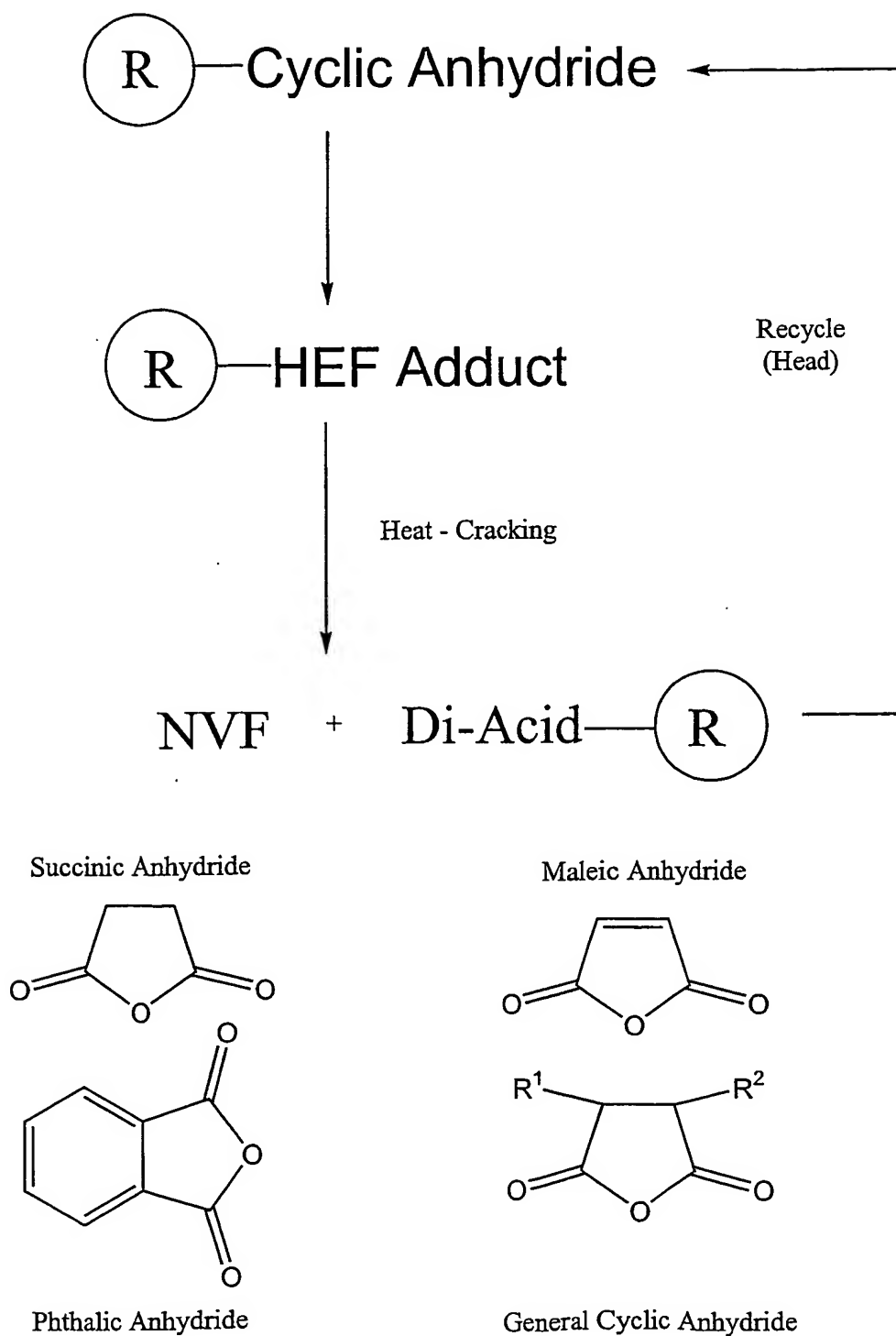
Fig. 1

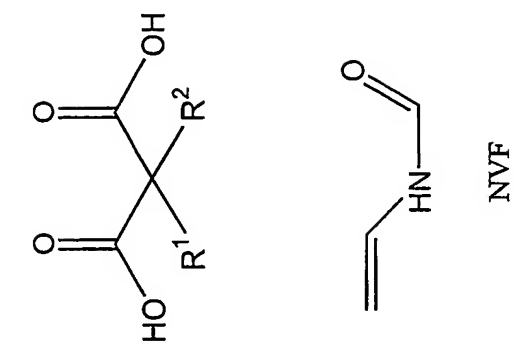
Fig. 2



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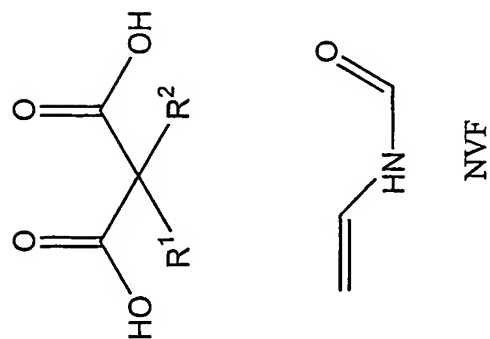
Fig. 3A





NVF

Fig. 3B



NVF

Fig. 3C

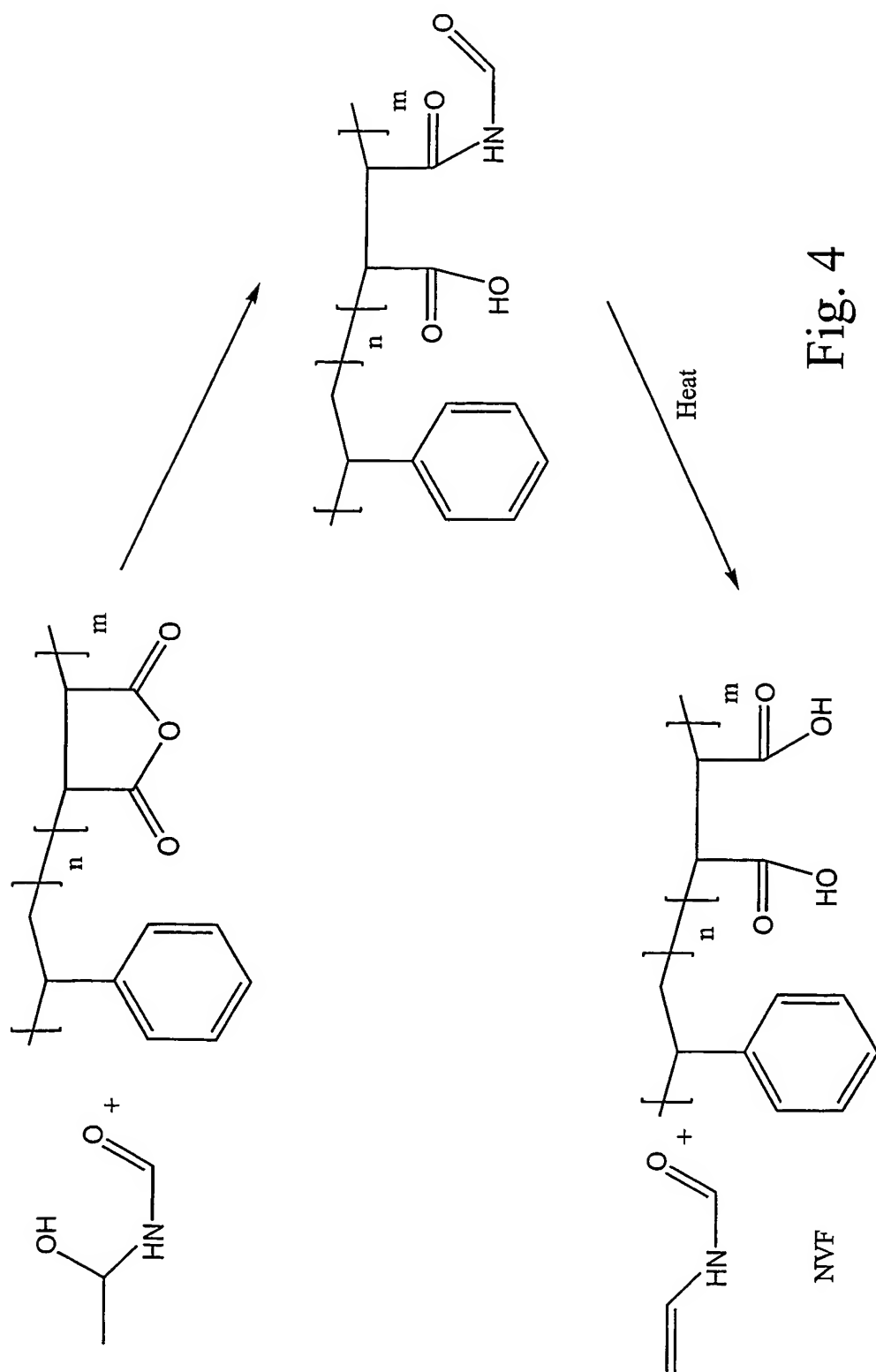


Fig. 5A

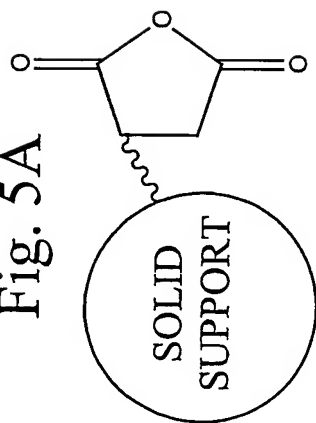
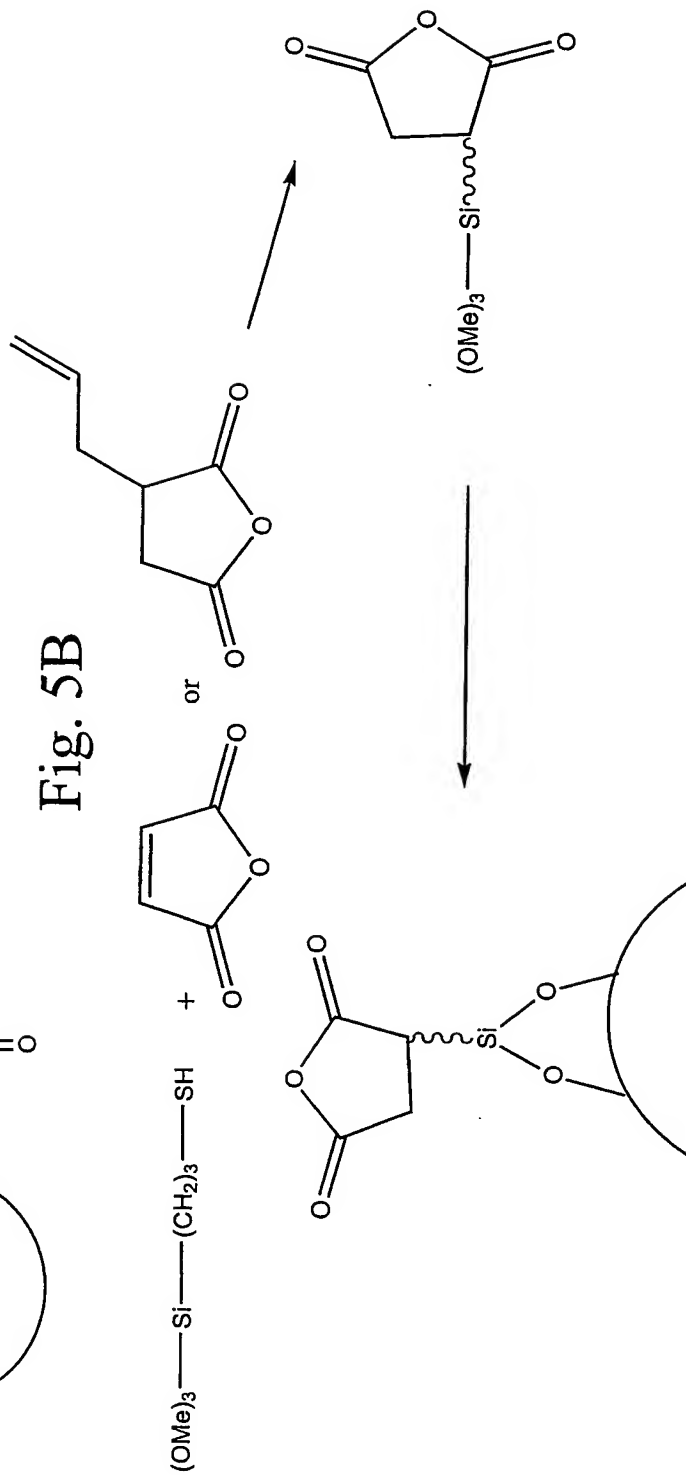


Fig. 5B



INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 03/27084

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C231/12 C07C233/03 C07F7/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 558 156 A (MITSUBISHI CHEM IND) 19 July 1985 (1985-07-19) claims 1-15; example 1 ---	1
A	PATENT ABSTRACTS OF JAPAN vol. 010, no. 276 (C-373), 10 September 1986 (1986-09-10) & JP 61 097309 A (MITSUBISHI CHEM IND LTD), 15 May 1986 (1986-05-15) abstract --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

18 December 2003

Date of mailing of the international search report

13/01/2004

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Authorized officer

Rufet, J

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 03/27084

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 200263 Derwent Publications Ltd., London, GB; Class E16, AN 1994-354704 XP002265612 & JP 03 319007 B (MITSUBISHI KASEI CORP), 26 August 2002 (2002-08-26) abstract</p> <p>----</p>	1
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X	<p>EP 0 361 514 A (FUJI PHOTO FILM CO LTD) 4 April 1990 (1990-04-04) pages 21, 25, 26; claim 1</p> <p>----</p>	30
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X	<p>EP 0 440 226 A (FUJI PHOTO FILM CO LTD) 7 August 1991 (1991-08-07) page 18 -page 23; claim 1</p> <p>-----</p>	30

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 03/27084

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 30 partly, 31 partly
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 30 partly, 31 partly

Present claims 30 and 31 relate to an extremely large number of possible products (reagent). Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the products claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the products according to page 10, last paragraph to page 11.

It is also stressed that the initial phase of the search revealed a very large number of documents relevant to the issue of novelty (see search report). So many documents were retrieved that it is impossible to determine which parts of the claims may be said to define subject-matter for which protection might legitimately be sought (Article 6 PCT). For these reasons, a meaningful search over the whole breadth of the claims 30 and 31 is impossible. Consequently, the search has been restricted as abovementioned

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/27084

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